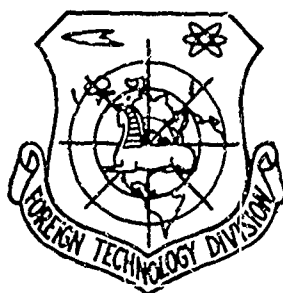# FOREIGN TECHNOLOGY DIVISION

STUDY OF BINARY OXIDES OF URANIUM AND RARE-EARTH ELEMENTS

by

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STUDY OF BINARY OXIDES OF URANIUM AND RARE-EARTH
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ABSTRACT

The formation of fluorite-type phases was investigated in $R_2O_3-U_3O_8-O_2$ systems (where R-La, Sm, Dy, Yb) annealed for 66-85 hr at 1200°C, and the solubility limits of the rare earth oxides in uranium octoxide were determined. The U(VI) content and the total uranium content were determined by coulometric analysis at a controlled potential. X-ray phase analysis was carried out by using the powder method with RKD-57 and RKU-86 cameras. The degree of oxidation of uranium changes with the ratio R/U and reaches 6 in samples where R/U=2/1. Thus, the presence of a rare earth oxide increases the stability of the hexavalent state of uranium at high temperatures. Contrary to expectations, the solubility of rare earth oxides in U_3O_8 was found to be very low (less than 1.5 mol % of $RO_{1.5}$).

Orig. art. has: 2 tables.

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STUDY OF BINARY OXIDES OF URANIUM AND RARE-EARTH ELEMENTS

G. G. Koshcheyev, L. M. Kovba, and A. V. Zhelankin

The $R_2O_3-U_3O_8$ (R—rare-earth element) systems were first studied by Hund et al. [1], who established phases with a fluorite-type structure in these systems. They consider that the valence state of uranium in the fluorite phase is the same as in U_3O_8, although this was not shown by chemical analysis. They did not study the solubility of R_2O_3 in uranous-uranic oxides, although the latter is of definite interest.

We studied the formation of fluorite phases in $R_2O_3-U_3O_8-O_2$ systems (where R is La, Sm, Dy or Yb) and determined the limits of the solubility of rare-earth oxides in uranous-uranic oxide.

The method of preparing the samples. The initial materials were "pure" uranium trioxide, "pure for analysis" lanthanum acetate, samarium oxide with >99.83% of the basic substance, dysprosium oxide (>99.7%) and ytterbium oxide (>99.8%). We prepared solutions of the nitrates of these oxides. The content of uranium in the solutions was determined by the weight method in the form of U_3O_8, and the content of the rare-earth elements was determined by the volume method, titration of the excess Trilon B in a solution of ammonium oxalate by potassium nitrate. Accurately determined quantities of the solutions were mixed together, and with intensive mixing we conducted joint deposition of ammonium diuranate and the hydroxide of the corresponding rare-earth element by mixing with ammonium that was free from carbonic acid. Preliminary annealing of the deposits at 700° for 4—6 h led to decomposition of the hydroxide and ammonium diuranate. The final annealing was conducted at 1200° in a Silit shaft furnace for 16—110 h.

In the prepared samples the U(VI) content and the total uranium content were determined by coulometric analysis at a controlled potential. X-ray phase analysis was carried out by the powder method in RKD-57 and RKU-86 cameras with CuK_{α} radiation for La and Yb, FeK_{α}

radiation for Sm, and CoK$_\alpha$ radiation for Dy. To determine the solubility limits of the rare-earth oxides in uranous-uranic oxide we used the focusing camera-monochromator, which gives high resolution.

The results of x-ray phase analysis and the chemical analysis are given in Tables 1 and 2.

Table 1. Results of the X-Ray Phase Analysis

Series La:U.

Ratio R:U	Mol.% R:U	$\tau_1 = 16{,}5$	$\tau_2 = 66$	$\tau_3 = 91$	Phase composition
1:278	0,36:99,64	—	—	—	$U_3O_8 + \beta U_3O_8$
1:56	1,76:98,24	—	—	—	$U_3O_8 + \beta U_3O_8 + (ULa)O_{2+x}$
1:10	9,1 :91,9	$5{,}471_6 \pm 0{,}0005$	$5{,}464 \pm 0{,}002$	—	$U_3O_8 + (ULa)O_{2+x}$
1:4,5	18,2 :81,8	$5{,}472_3 \pm 0{,}0005$	$5{,}469_4 \pm 0{,}0005$	—	$U_3O_8 + (ULa)O_{2+x}$
1:3	25 :75	$5{,}472_2 \pm 0{,}0005$	$5{,}467_3 \pm 0{,}0005$	—	$(ULa)O_{2+x} + U_3O_8$
1:1,5	40 :60	$5{,}491_6 \pm 0{,}0005$	$5{,}490_3 \pm 0{,}0005$	$5{,}472_4 \pm 0{,}0005$	$(ULa)O_{2+x}$
1:1	50 :50	$5{,}519_2 \pm 0{,}0005$	$5{,}515_5 \pm 0{,}0005$	—	$(ULa)O_{2+x}$
2:1	66,7 :33,3	$5{,}564_3 \pm 0{,}0005$	$5{,}560_3 \pm 0{,}0005$	$5{,}562_3 \pm 0{,}0005$	$(ULa)O_{2+x}$

Series Sm:U.

Ratio R:U	Mol.% R:U	$\tau_1 = 17{,}5$	$\tau_2 = 84$	$\tau_3 = 109$	Phase composition
1:312	0,32:99,68	—	—	—	$U_3O_8 + \beta U_3O_8$
1:61	1,64:98,36	—	—	—	$U_3O_8 + (USm)O_{2+x}$
1:10	9,1 :91,9	$5{,}420 \pm 0{,}001$	$5{,}416 \pm 0{,}02$	—	$U_3O_8 + (USm)O_{2+x}$
1:4,5	18,2 :81,8	$5{,}417 \pm 0{,}001$	—	—	$U_3O_8 + (USm)O_{2+x}$
1:3	25 :75	$5{,}416 \pm 0{,}001$	$5{,}415 \pm 0{,}001$	—	$(USm)O_{2+x} + U_3O_8$
1:1,5	40 :60	$5{,}417 \pm 0{,}001$	$5{,}415 \pm 0{,}001$	—	$(USm)O_{2+x}$
1:1	50 :50	$5{,}411 \pm 0{,}001$	$5{,}414 \pm 0{,}001$	—	$(USm)O_{2+x}$
2:1	66,7 :33,3	$5{,}414 \pm 0{,}001$	$5{,}415 \pm 0{,}001$	$5{,}414 \pm 0{,}001$	$(USm)O_{2+x}$

lattice parameters in Å as a function of annealing time in h

Table 1. (Continued)

Ratio R:U	Mol.% R:U	Lattice parameters in Å as a function of annealing time in h				Phase composition
		τ_1	τ_2	τ_3	τ_5	
Series Dy:U		$\tau_1=18{,}5$		$\tau_3=85$	$\tau_5=110$	
1:333	0,3 :99,7	—		—	—	$U_3O_8+\beta U_3O_8$
1:65	1,54:98,46	—		$5{,}366\pm0{,}002$	—	$U_3O_8+(UDy)O_{2+x}$
1:10	9,1 :91,9	$5{,}360_6\pm0{,}0005$		—	—	$U_3O_8+(UDy)O_{2+x}$
1:4,5	18,2 :81,8	—		$5{,}367_4\pm0{,}0005$	—	$U_3O_8+(UDy)O_{2+x}$
1:3	25 :75	—		$5{,}366_4\pm0{,}0005$	—	$(UDy)O_{2+x}+U_3O_8$
1:1,5	40 :60	$5{,}365_3\pm0{,}0005$		$5{,}366_0\pm0{,}0005$	$5{,}366_3\pm0{,}0005$	$(UDy)O_{2+x}+U_3O_8$
1:1	50 :50	—		$5{,}360_1\pm0{,}0005$	—	$(UDy)O_{2+x}$
2:1	66,7 :33,3	$5{,}338_3\pm0{,}0005$		$5{,}339_6\pm0{,}0005$	$5{,}337_6\pm0{,}0005$	$(UDy)O_{2+x}$
Series Yb:U		$\tau_1=22{,}5$		$\tau_3=76{,}5$	$\tau_5=101{,}5$	
1:68	1,46:98,54	—		$5{,}319\pm0{,}002$	—	$U_3O_8+(UYb)O_{2+x}$
1:10	9,1 :91,9	—		$5{,}319_4\pm0{,}0005$	—	$U_3O_8+(UYb)O_{2+x}$
1:4,5	18,2 :81,8	$5{,}313_3\pm0{,}0005$		$5{,}319_4\pm0{,}0005$	$5{,}321_8\pm0{,}0005$	$U_3O_8+(UYb)O_{2+x}$
1:3	25 :75	$5{,}319_4\pm0{,}0005$		$5{,}318_3\pm0{,}0005$	$5{,}318_4\pm0{,}0005$	$(UYb)O_{2+x}+U_3O_8$
1:1,5	40 :60	$5{,}319_4\pm0{,}0005$		$5{,}314_3\pm0{,}0005$	—	$(UYb)O_{2+x}+U_3O_8$
1:1	50 :50	—		—	—	$(UYb)O_{2+x}$
2:1	66,7 :33,3	$5{,}273_3\pm0{,}0005$		$5{,}273_3\pm0{,}0005$	$5{,}273_4\pm0{,}0005$	$(UYb)O_{2+x}$

Table 2. Results of the Coulometric Analysis to Determine the O/U Ratios

Ratio R:U	Mol.% R:U	Series			
		La:U τ 66 h	Sm:U τ 84 h	Dy:U τ 85 h	Yb:U τ 76,5 h
	0,2*:99,8	2,42±0,03	2,57±0,03	2,55±0,03	
	1,0*:99,0				2,63±0,03
1:10	9,1:91,9	2,70±0,03	2,63±0,03	2,69±0,03	2,63±0,03
1:3	25:75	2,58±0,03	2,53+0,03	2,66±0,03	2,63±0,03
1:1,5	40:60	2,58±0,03	2,61±0,03	2,51±0,03	2,63±0,03
1:1	50:50	2,66±0,03	2,53±0,03	2,54±0,03	2,53±0,03
2:1	66,7:33,3	2,88±0,03	2,86±0,03	2,83±0,03	2,93±0,03

* In wt. %

In the samples annealed at 1200° for 66–85 h we determined the O/U ratio coulometrically from the $U(VI)/U_{total}$, from which we calculated the chemical composition. The analysis supported the constancy of the compositions of the given R/U ratios.

As is evident from Tables 1 and 2, the degree of oxidation of uranium changes with the R/U ratio and attains six in samples where R/U = 2/1, which supports Hill's assumption [3]. Thus, the presence of a rare-earth oxide increases the stability of the hexavalent state of uranium at high temperatures, and the conclusion made by Hochstra and Siegel [4] on the basis of Hund's works [1] is invalid.

Very interesting data were obtained in the study of the solubility. In view of the closeness of the dimensions of the rare-earth ions and the type of coordination one would expect noticeable solubility of their oxides in uranous-uranic oxide; in any case the conditions for the formation of solid solutions are more favorable here than in other U_3O_8-containing systems. As follows from Table 1, the solubility in U_3O_8 is very low (less than 1.5 mol. % of $RO_{1.5}$). Consequently, the other oxides cannot have noticeable solubility in uranous-uranic oxide.

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